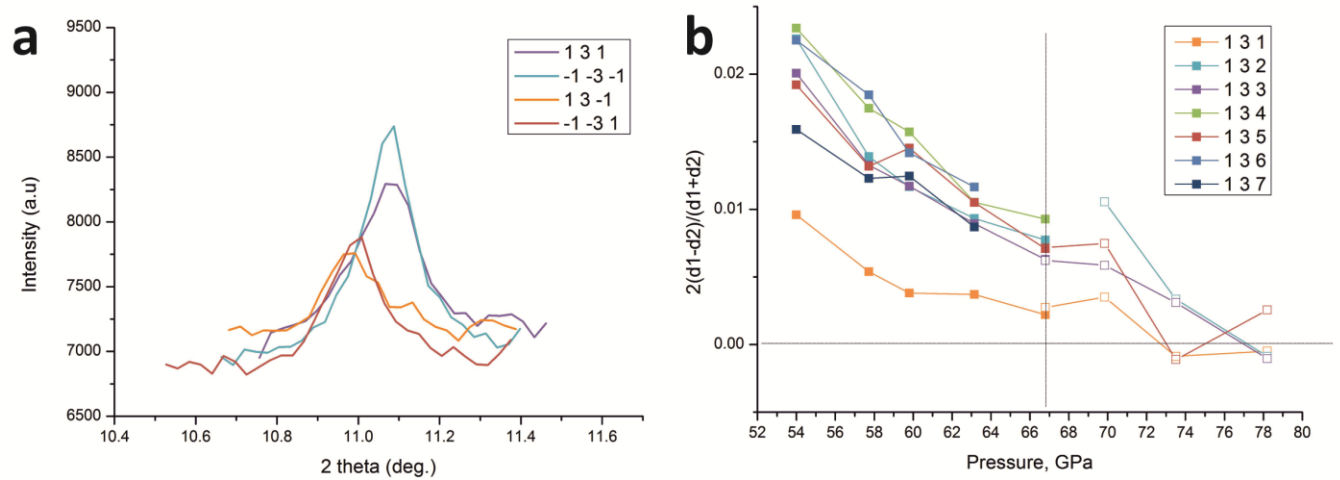
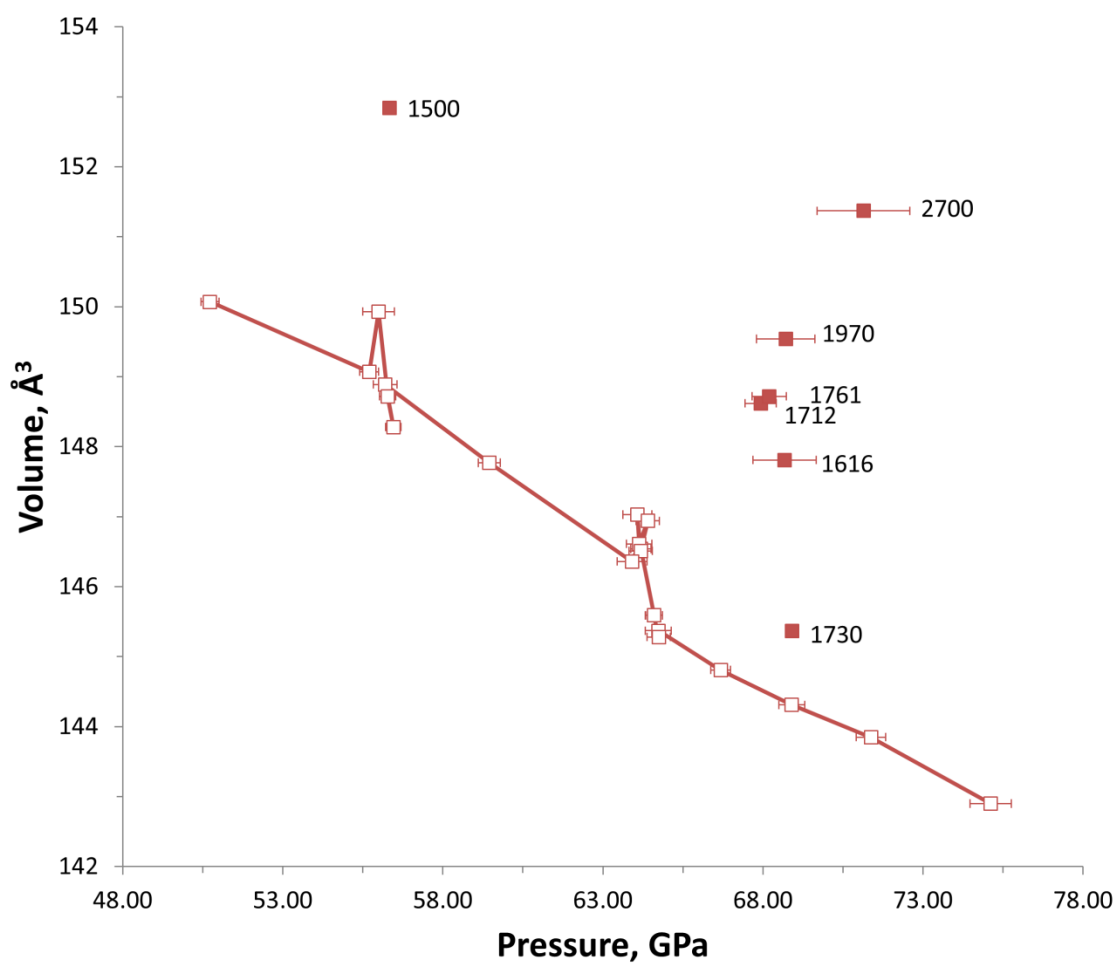


Supplementary Figure 1: P - V plot for Fe₂O₃ summarized from current experimental results. Unit cell volumes are normalized to the amount of structural units Z . Open symbols represent ambient-temperature experiments and solid symbols indicate samples subjected to laser heating. The volume relaxation of η -Fe₂O₃ under decompression shows apparent discontinuities after annealing at ~ 56 GPa and 64 GPa due to possible decomposition (see Supplementary Figure 3 for details). The volume of the high-temperature polymorph ι -Fe₂O₃ is lower than the volume of hematite at the identical pressure.

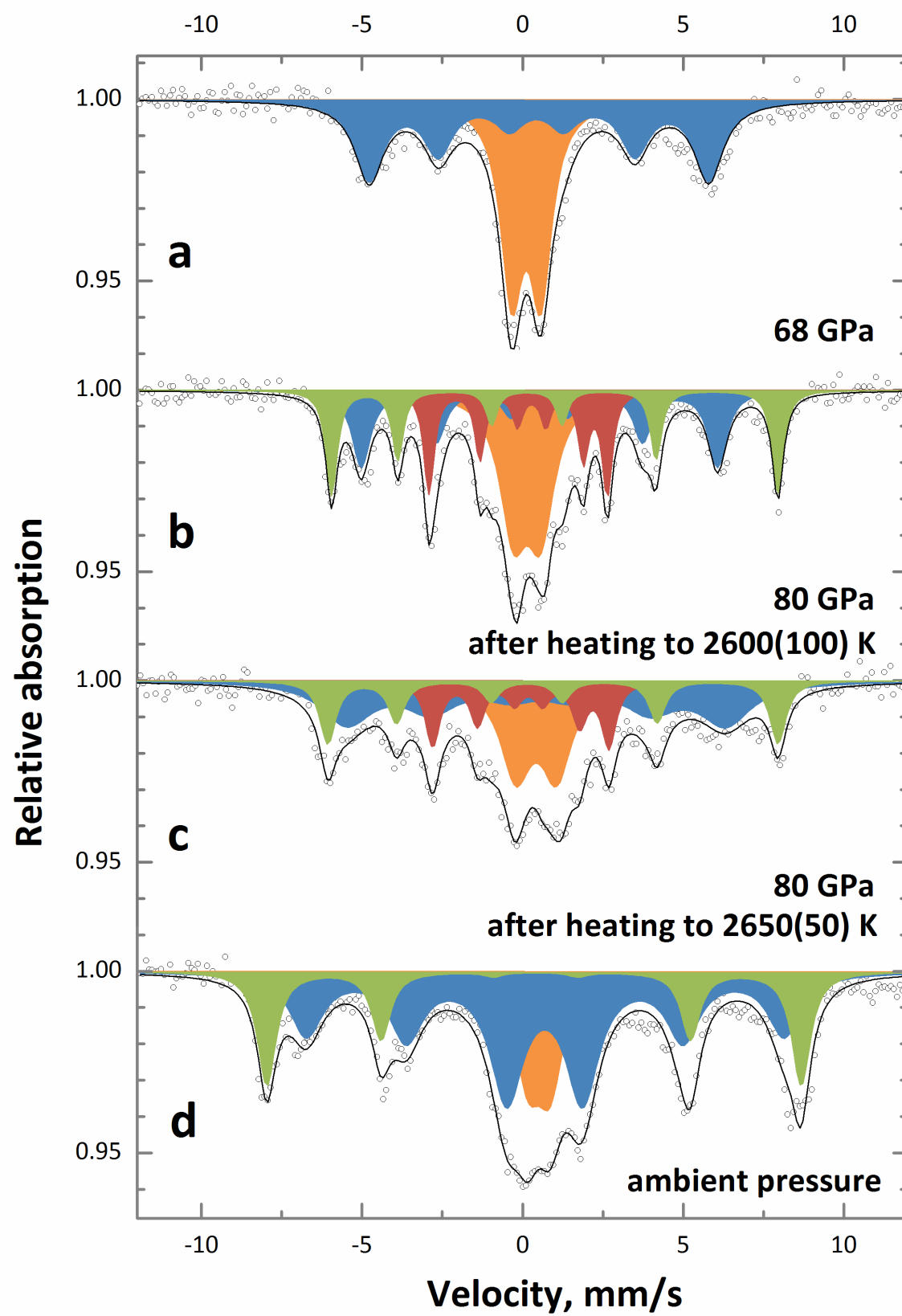


Supplementary Figure 2: Verification of the crystal system for ζ -Fe₂O₃. (a) We used one dimensional profiles of reflection 131 and its symmetrical equivalents in the hypothetical orthorhombic space group reconstructed from the wide image recorded at 60.0(7) GPa. While d -spacings for Friedel mates (131 and -1-3-1 / -1-31 and 13-1) show a perfect match, the first pair has smaller d -spacings (corresponding to $2\theta = 10.98^\circ$) than the second one ($2\theta = 11.08^\circ$). (b) The cumulative picture for reflections 13 l ($l = 1 \dots 7$) shows how the difference in d -spacings (normalized to corresponding sums) decreases under compression to half of its value before the phase transition to θ -Fe₂O₃ at 67 GPa (vertical dotted line) (see Supplementary Text for details).



Supplementary Figure 3: Unit cell volume of η -Fe₂O₃ under decompression and laser annealing.

The sequence of measurements goes from right to left. Numbers refer to the heating temperature with an average deviation of 100 K. Heating at ~56 GPa and 64 GPa provokes a unit cell volume increase of up to 1 % that is likely associated with the loss of oxygen by η -Fe₂O₃ and partial reduction of Fe³⁺ to Fe²⁺.



Supplementary Figure 4. Examples of Mössbauer spectra collected using a ^{57}Co source from 50% enriched $^{57}\text{Fe}_2\text{O}_3$ compressed in Ar pressure transmitting medium and laser-heated in DAC. (a) In $\zeta\text{-Fe}_2\text{O}_3$ at 68(4) GPa iron atoms are in a high-spin magnetic state (with centre shift (CS) of 0.453(9) mm/s, blue sextet) and in low-spin non-magnetic state (CS = 0.113(4) mm/s, orange doublet). (b) After first heating during about 10 min at 2600(100) K pressure increased to 80(5) GPa and spectrum changed drastically: it consists of four components – three magnetic sextets (with CS (mm/s) 0.570(4), green; 0.516(8), blue; 0.074(4), red), and doublet (CS 0.154(7) mm/s, orange). (c) Several times subsequent heating at 2650(50) K with total duration over 40 min did not result in pressure changes (80(5) GPa), but Mössbauer spectra underwent some modifications and eventually became as shown in the figure: they consist of four components - three magnetic sextets (with CS (mm/s) 0.539(7), green; 0.498(8), blue; 0.065(7), red), and a doublet (CS 0.423(10) mm/s, orange). (d) After decompression the spectrum consists of three components, two magnetic sextets (with CS (mm/s) 0.382(6), green; 0.697(9), blue) and one doublet (CS 0.513(16) mm/s, orange). Note that the hyperfine parameters of the ‘blue’ component in (d) coincide almost exactly with those of $\text{Fe}^{2.67+}$ (mixed valence state “B-position”) of magnetite at ambient conditions. The presence in the Mössbauer spectra (b, c, d) of components with high CS (above 0.5 mm/s) demonstrates that laser heating leads to partial reduction of Fe^{3+} and formation of Fe^{2+} or, more probably, a mixed valence state of iron ions.

Supplementary Table 1. Details of crystal structure refinements of high-pressure Fe₂O₃ phases

Crystallographic data	θ -Fe ₂ O ₃	η -Fe ₂ O ₃	η -Fe ₂ O ₃	ι -Fe ₂ O ₃
<i>P</i>, <i>T</i> conditions	73.8(7) GPa	63.9(5) GPa,	75.1(7) GPa	40.7(3) GPa,
of XRD experiment		after annealing at 2200(100) K	after annealing at 1850(100) K	after annealing at 1800(100) K
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Aba2</i>	<i>Cmcm</i>	<i>Cmcm</i>	<i>Pbcn</i>
<i>a</i> (Å)	6.524(9)	2.640(6)	2.6393(7)	7.062(10)
<i>b</i> (Å)	4.702(3)	8.639(9)	8.5177(15)	4.8108(13)
<i>c</i> (Å)	4.603(7)	6.414(14)	6.358(2)	5.0019(8)
<i>V</i> (Å³)	141.2(3)	146.3(5)	142.93(7)	169.9(2)
<i>Z</i>	4	4	4	4
<i>F</i>(000)	304	304	304	304
Theta range for data collection (°)	4.03 to 15.13	2.68 to 11.10	3.76 to 10.96	3.08 to 10.82
Completeness to <i>d</i> = 0.8 Å, %	45.0	69.3	61.6	48.0
Index ranges	-7 < <i>h</i> < 4, -5 < <i>k</i> < 5, -4 < <i>l</i> < 5	-2 < <i>h</i> < 2, -9 < <i>k</i> < 9, -6 < <i>l</i> < 5	-2 < <i>h</i> < 2, -9 < <i>k</i> < 9, -5 < <i>l</i> < 5	-2 < <i>h</i> < 4, -5 < <i>k</i> < 5, -5 < <i>l</i> < 5
Reflections collected	54	93	81	206
Independent reflections / <i>R</i>_{int}	45 / 0.0329	53 / 0.0637	46 / 0.0372	61 / 0.1003
Refinement method	Full matrix least squares on <i>F</i> ²			
Data / restraints / parameters	45 / 1 / 12	53 / 0 / 9	46 / 0 / 9	61 / 0 / 16
Goodness of fit on <i>F</i>²	1.236	1.212	1.173	1.248
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0943 / 0.1669	0.0654 / 0.1635	0.0860 / 0.2101	0.0755 / 0.1942

Crystallographic data	θ -Fe ₂ O ₃	η -Fe ₂ O ₃	η -Fe ₂ O ₃	ι -Fe ₂ O ₃
R_1 / wR_2				
<i>R</i> indices (all data) R_1 / wR_2	0.1058 / 0.1736	0.0910 / 0.1806	0.0909 / 0.2132	0.0847 / 0.1986
Largest diff. peak /hole (<i>e</i> / Å ³)	1.425 / -1.786	1.851 / -1.416	1.730 / -2.432	1.283 / -1.097
ICSD reference N	430557	430558	430559	430560

Supplementary Table 2. Details of crystal structure refinements of Fe₅O₇ and Fe₂₅O₃₂

Crystallographic data	Fe ₅ O ₇	HP-Fe ₃ O ₄	Fe ₂₅ O ₃₂
<i>P</i>, <i>T</i> conditions	40.7(3) GPa,	44.3(5) GPa,	80.1(5) GPa,
of XRD experiment	after annealing of Fe ₂ O ₃ at 1800(100) K	after annealing of Fe ₃ O ₄ at 2350(100) K	after annealing of Fe ₃ O ₄ at 2950(100) K
Crystal system	Monoclinic	Orthorhombic	Hexagonal
Space group	<i>C2/m</i>	<i>Bbmm</i>	<i>P-62m</i>
<i>a</i> (Å)	9.208(7)	9.309(3)	13.4275(16)
<i>b</i> (Å)	2.7327(10)	9.282(2)	13.4275(16)
<i>c</i> (Å)	8.270(5)	2.6944(9)	2.6289(4)
α (°)	90	90	90
β (°)	105.50(8)	90	90
γ (°)	90	90	120
<i>V</i> (Å³)	200.5(2)	232.80(11)	410.48(12)
<i>Z</i>	2	4	1
<i>F</i>(000)	372	440	906
Theta range for data collection (°)	2.77 to 10.78	3.57 to 11.05	3.32 to 15.47
Completeness to <i>d</i> = 0.8 Å, %	39.2	82.5	91.3
Index ranges	-8 < <i>h</i> < 9, -2 < <i>k</i> < 2, -8 < <i>l</i> < 9	-10 < <i>h</i> < 10, -11 < <i>k</i> < 10, -3 < <i>l</i> < 3	-17 < <i>h</i> < 18, -18 < <i>k</i> < 18, -3 < <i>l</i> < 3
Reflections collected	106	517	2353
Independent reflections / <i>R</i>_{int}	72 / 0.0385	123 / 0.0544	487 / 0.1009
Refinement method	Full matrix least squares on <i>F</i> ²		
Data / restraints / parameters	72 / 0 / 18	123 / 0 / 17	487 / 0 / 50
Goodness of fit on <i>F</i>²	1.056	1.253	1.086

Final R indices [$I > 2\sigma(I)$],	0.0638 / 0.1541	0.0686 / 0.1649	0.0547 / 0.1257
R_1 / wR_2			
R indices (all data),	0.0673 / 0.1583	0.0691 / 0.1649	0.0805 / 0.1369
R_1 / wR_2			
Largest diff. peak /hole	1.126 / -1.001	2.263 / -1.621	1.569 / -1.396
($e / \text{\AA}^3$)			
ICSD reference N	430563	430561	430562

Supplementary Note 1. Verification of ζ -Fe₂O₃ crystal system

Following our previous study¹ we verified the symmetry of the unit cell by inspecting d -spacings of those reflections that should have been equivalent in orthorhombic symmetry but differed in lower symmetries. It should be noted that previous powder diffraction studies were not able to resolve such differences due to the strong broadening of closely overlapping reflections. In single crystal XRD the overlapping problem is solved since the reflections are located at different places on the frames and their d -spacings could be measured separately.

The absence of orthorhombic symmetry can be clearly demonstrated by considering sets of candidate reflections $13l$ ($l = 1, 2, \dots, 7$) with the following equivalents: $13l$, $-1-3l$, $13-l$ and $-1-3-l$. Supplementary Figure 2a shows that the $-1-31$ and $13-1$ reflections have larger d -spacings than the 131 and $-1-3-1$ ones. There is a perfect match in d -spacings between Friedel mates (131 and $-1-3-1$ / $-1-31$ and $13-1$) indicating negligible effects of strain created by the DAC.

A verification of the monoclinic unit cell using a similar approach was hindered due to the lack of equivalent reflections for the particular symmetry defined by the specific orientation of the crystal in the DAC. Therefore we refined the unit cell based on the available reflections without symmetry constraints, i.e., a triclinic cell. As a result the alpha and beta angles show systematic scatter from 90° of about 0.4° while gamma varies by much less, $\sim 0.1^\circ$. The overall scatter, representing the distortion from the orthorhombic perovskite type, is demonstrated in Supplementary Figure 2b, where it is expressed as the difference between d -spacings of the close reflections normalized to their sum.

Supplementary Note 2. Notes on high pressure behavior of Fe₃O₄

Single crystals of synthetic magnetite Fe₃O₄² were studied in double-side laser heated DACs at pressures up to 80 GPa and over 3000 K. Results of the study will be published elsewhere. Our single-crystal synchrotron XRD study of magnetite at ambient temperature confirmed the phase transition between 29 and 31 GPa and the CaTi₂O₄-type structure (space group *Bbmm*, No. #63) of the high-pressure *HP*-Fe₃O₄ phase (Fig. 4). Laser heating of *HP*-Fe₃O₄ at 2350(100) K and pressures up to 50 GPa does not result in any chemical or structural modifications (Supplementary Table 2). Evidence for the existence of the *HP*-Fe₃O₄ phase at even higher P,T conditions was found in our independent experiments on siderite (FeCO₃). By studying products of its decomposition after treatment at 70(1) GPa and 2400(100) K, we identified reflections in the XRD pattern that belong to *HP*-Fe₃O₄.

Upon heating at 80(1) GPa and 2950(100) we observed formation of a new phase with hexagonal unit cell (space group *P-62m*, No. #189). Structure solution from the single-crystal data revealed that the phase is a new iron oxide with composition Fe₂₅O₃₂ (Supplementary Table 2). Similar to iron oxides

belonging to the $n\text{FeO} \cdot m\text{Fe}_2\text{O}_3$ homological series, $\text{Fe}_{25}\text{O}_{32}$ is a quasi-two-dimensional structure constructed of parallel columns of triangular face-shared prisms and edge-shared octahedra, but has in additional columns of edge-shared one-capped prisms (Fig. 1g).

Supplementary References

1. Bykova, E. *et al.* Novel high pressure monoclinic Fe_2O_3 polymorph revealed by single-crystal synchrotron X-ray diffraction studies. *High Pressure Res.* **33**, 534–545 (2013).
2. Glazyrin, K. *et al.* Effect of high pressure on the crystal structure and electronic properties of magnetite below 25 GPa. *Am. Mineral.* **97**, 128–133 (2012).